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Simulation of clusters formation in Al-Cu based and Al-Zn based alloys

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A Monte Carlo computer simulation is adopted to investigate the role of micro-alloying elements Mg and Ag in Al-Cu and Al-Zn alloys. Small amount additions of Mg to the Al-Cu alloy markedly retard the formation of Cu clusters due to the preferential trapping of free-vacancies available for Cu diffusion. On the other hand, additions of Mg to the Al-Zn alloy promote the formation of Zn clusters due to the preferential Mg-Zn interaction. As for the effect of Ag, it is found that, in both Al-Cu-Mg and Al-Zn-Mg alloys, Ag atoms are preferentially bounded to Mg-Cu-vacancy or Mg-Zn-vacancy complexes. However, in Al-Cu-Mg alloy Ag atoms interact with Mg, while in Al-Zn-Mg alloy they interact with both Mg and Zn.

1. Introduction

The effect of micro-alloying elements on the behavior of age-hardenable alloys is an interesting physical problem addressing the mechanisms of transport and aggregation of the solute, which has important technological applications (such as optimization of the thermal treatments, nucleation of precipitates, stability of the microstructure, etc.). Special attention has been given in the literature to the effect of Mg and Ag in Al-Cu and Al-Zn based alloys from a viewpoint of industrial significance.

The addition of small amounts of Mg and Ag into Al-Cu alloy with high Cu: Mg ratio will modify the sequence of precipitation and induce the formation of Ω phase of disc shape on {111} planes rather than on {001} planes [1]. Reich *et al.* [2] demonstrated that Mg-Ag co-clusters occur first during artificial aging without well-defined shape detected by atom probe field ion microscope (APFIM). As Cu atoms join in these co-clusters, they grow on {111} planes with the shape tending to be plate-like. These precipitates are designated as {111} GP zones. These plate-like particles on the {111} planes of matrix grow along the lateral directions by subsequent aging showing structural features as the Ω phase. The addition of small amount of Ag to Al-Zn-Mg alloys has been reported to increase both the rates of hardening and the peak values, and indirect evidence suggested that these effects might arise from a preferential interaction between Ag atom (possibly in conjunction with Mg atom) and vacancy, which stimulates the nucleation of the intermediate precipitate η' [3–5]. More recently, APFIM studies on the same alloys [6] had revealed the early clustering of Zn and Ag atoms to be also significant. Although indirect observations suggest the effect of Ag may be originated from a preferential interaction between Ag, Mg atoms and vacancies during, or immediately after, quenching from the solution treatment temperature, however, the precise atomic behavior of Ag and Mg in Al-Cu and Al-Zn based alloys remains unknown due to the difficulty of direct detection of atomic behavior using any available experimental methods. Therefore, a theoretical approach using reasonable models becomes extremely necessary in predicting the fundamental role of micro-alloying Mg and Ag in Al-Cu based and Al-Zn based alloys.

Recently, Sato *et al.* [7] successfully classified the role of various microalloying elements during the phase transformation of Al-Li and Al-Cu alloys using a Monte Carlo computer simulation. This simulation method has proved to be capable of spatially and temporally reproducing atomistic behaviors occurring in alloys. More recently, Zhu *et al.* [8] investigated trace element effects on precipitation in Al-Cu-Mg-(Ag, Si) alloys using a multi-component quasi-chemical model in which short-range-order parameters were calculated based on CALPHAD databases. However, the results of Zhu *et al.* are based on static analysis since they did not consider the exchange of atoms. In this work, a computer simulation on the diffusion of solute atoms, nucleation and growth of precipitates etc. using a Monte Carlo method similar to the method of Sato *et al.* was applied to both Al-Cu and Al-Zn based alloys containing micro-alloying elements Mg and Ag. All the utilized simulation parameters, which significantly affect the obtained results, were derived from known thermodynamic and kinetic data.

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TABLE I Chemical composition of studied alloys (mol%)

Alloys	Cu	Zn	Mg	Ag	Al
1	1.8	–	–	–	Bal
2	1.8	–	–	0.1	Bal
3	1.8	–	0.5	–	Bal
4	1.8	–	0.5	0.1	Bal
5	–	1.8	–	–	Bal
6	–	1.8	–	0.3	Bal
7	–	1.8	3.2	–	Bal
8	–	1.8	3.2	0.3	Bal

2. Simulation model

2.1. Simulation method

The computer simulations were performed on a rigid three-dimensional FCC lattice with 50 × 50 × 51 unit cells by a conventional Monte Carlo method. Periodic boundary conditions were also adopted to eliminate the limitation of the above simulation size. As an initial microstructure of the simulation system, all the lattice sites are occupied randomly by Al, Cu or Zn and other elemental atoms determined by the corresponding alloy compositions. The chemical compositions of the alloys are listed in Table I. The realistic diffusion of these atoms takes place via vacancies with the concentration of $\sim 1.5 \times 10^{-4}$, which approximately agrees with the equilibrium vacancy concentration in pure Al at 793 K. This postulates that the investigated phase transformations evolve without diminishing the quenched-in excess vacancies during the simulations. The exchange of randomly selected vacancy with one of its nearest neighbor atoms is allowed if the transition probability, W, is greater than a randomly generated number between 0 and 1, x. The value of W is calculated from the symmetrical solution [9]:

$$W = \exp(-\Delta E/RT)/[1 + \exp(-\Delta E/RT)], \quad (1)$$

where ΔE is the energy difference between the atomic configurations before and after the exchange, R the gas constant and T the temperature for simulation.

In this paper, a Monte Carlo step is defined as an attempt exchange of atom and vacancy. The Monte Carlo step can be roughly related to the real time by considering the average vibration frequency of the atoms approximately. Some structural parameters characterizing the simulation microstructures were recoded as a function of Monte Carlo steps. Three statistically independent runs were performed for each alloy type for averaging purposes. A cluster was defined as a solute atom aggregate containing two or more than two solute atoms. Therefore, residual solute concentration in the matrix is estimated as a concentration of the isolated solute atoms surrounded by Al atoms. Average size of clusters is defined as the average number of atoms inside one cluster. The probability of solute A-solute B pair is defined as:

$$P(A|B) = \frac{P(AB)}{P(B) \times Z} = \frac{P_{A-B}}{C_B \times Z},$$

where $P(AB)$ is the number of solute A-solute B pair, C_{B} is the molar fraction of B atom and Z is the coordination number.

TABLE II Pair interactions utilized for simulations (in KJ/mol)

	Al	Cu	Mg	Zn	Ag	Vacancy
Al	−54.5	−49.3	−34.5	−36.4	−49.6	−21.9
Cu	–	−48.5	−32.2	−33.4	−45.5	−15.8
Mg	–	–	−16.8	−31.0	−34.6	−10.3
Zn	–	–	–	−20.3	−32.3	−6.1
Ag	–	–	–	–	−47.3	−14.8
Vacancy	–	–	–	–	–	0

Moreover, we did not consider the elastic effect induced by the difference in atomic radiu among different atoms. This simplification has some influence on the morphologies of precipitates, but it is reasonable because the formation of clusters in Al alloys is generally believed to be governed by the rate of the diffusion-controlled growth rather than that of the interface-controlled growth.

2.2. Simulation parameters

The study of cluster formations using a Monte Carlo method requires an accurate estimation of interaomic interactions in alloys. In this work, the utilized pair interactions were derived from known thermodynamic or kinetics quantities such as the cohesive energy E_{coh}, the formaion energy of a vacancy E_V^F, and the nearest neighbor interatomic distance r_{ii}^{pure} in pure metal i together with the values of maximum solubility limits $C_j^{\max}$ and the corresponding temperatures $T_j^{\max}$ in equilibrium phase diagrams. The utilized pair interactions for the Monte Carlo simulation are summarized in Table II. The detailed derivation method of simulation parameters is as follows.

Pair interaction between same atom species, ε_{ii}, is estimated from the phenomenological Lennard-Jones type potential of the following form:

$$\varepsilon_{ii} = \varepsilon_{ii}^{\mathrm{pure}}\left[\left(r_{ii}^{\mathrm{pure}}/r_{\mathrm{AlAl}}^{\mathrm{pure}}\right)^8 - 2\left(r_{ii}^{\mathrm{pure}}/r_{\mathrm{AlAl}}^{\mathrm{pure}}\right)^4\right] \quad (2)$$

where a pair interaction between i-i atoms in the pure metal is evaluated as

$$\varepsilon_{ii}^{\mathrm{pure}} = 2E_{\mathrm{coh}}/Z \quad (3)$$

where E_{coh} and Z are cohesive energy and coordination number, respectively. The exponents of repulsive and attractive terms in Equation 2, i.e. 8 and 4 are average values for pure metals [10, 11].

In contrast, pair interaction between different atom species ε_{ij} can be obtained by:

$$\varepsilon_{ij} = \varepsilon_{\mathrm{dia}} + (\varepsilon_{ii} + \varepsilon_{jj})/2 \quad (4)$$

where $\varepsilon_{\mathrm{dia}}$ named as order parameter can be derived from the corresponding i-j equilibrium phase diagrams under a regular solution approximation [10]:

$$\varepsilon_{\mathrm{dia}} + RT_j^{\max}\left[\ln\left(1 - c_j^{\max}\right) - \ln c_j^{\max}\right] / N_a Z\left(1 - 2c_j^{\max}\right) \quad (7)$$

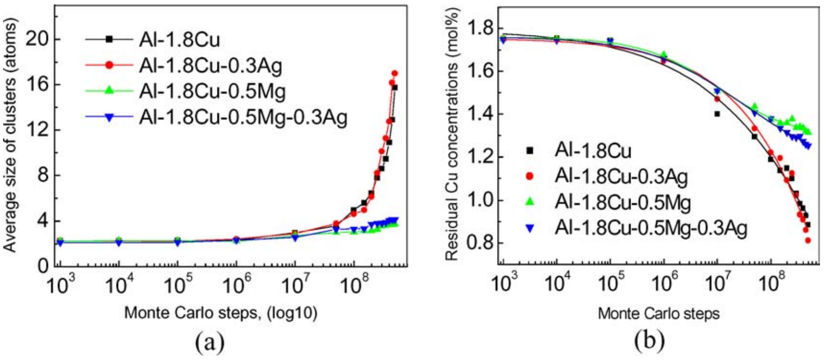


Figure 1 Variations of average size of Cu clusters (a) and residual Cu concentrations in the matrix (b) with Monte Carlo steps for Al-Cu (-Mg-Ag) alloys simulated at 453 K.

Pair interaction between an atom and a vacancy, ε_{iV}, is estimated from the assumed potential (i.e. 0-1 type Lennard-Jone potential) of the form:

$$\varepsilon_{iV} = -\varepsilon_{iV}^{\text{pure}}\left(r_{ii}^{\text{pure}}/r_{\text{AlAl}}^{\text{pure}}\right) \tag{8}$$

Here, the 'ghost' pair interaction between an atom and a vacancy in the pure metal, $\varepsilon_{iv}^{\text{pure}}$, is evaluated from

$$\varepsilon_{iV}^{\text{pure}} = \left(E_V^F + E_{\text{coh}}\right)/Z \tag{9}$$

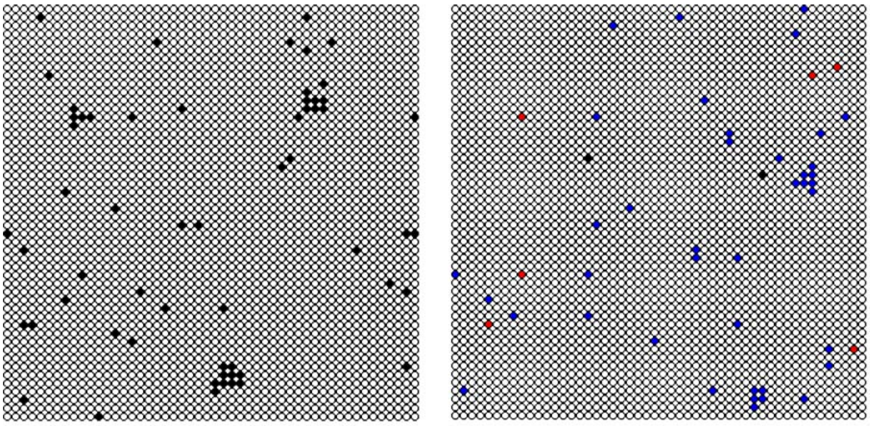
as derived by Doyam *et al.* [13].

The method is fit for the elements having the fcc structures. It is not true to be adopted to simulate the behaviors of other structural elements such as Si. All the parameters are assumed to be independent of both the composition and temperature of simulated alloys.

3. Results and discussion

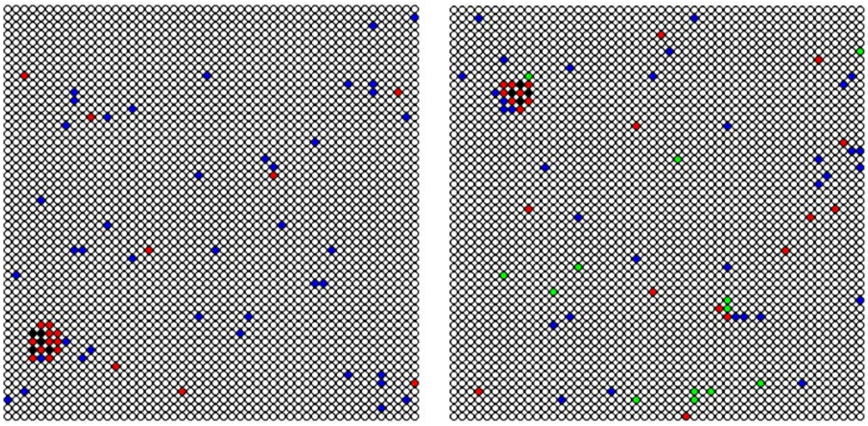
3.1. Al-Cu based alloys

Al-Cu is the most widely studied age hardening alloy, several alloys based on this system are under developing for industrial use. However, some effects of



(a) Black circle represents Cu atom

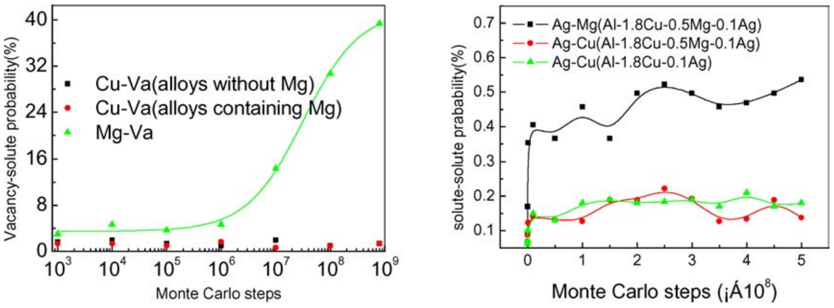
(b) blue, red and black circles represent Cu, Ag atoms and vacancies respectively



(c) Blue, red, black circles represent Cu, Mg atoms and vacancies respectively

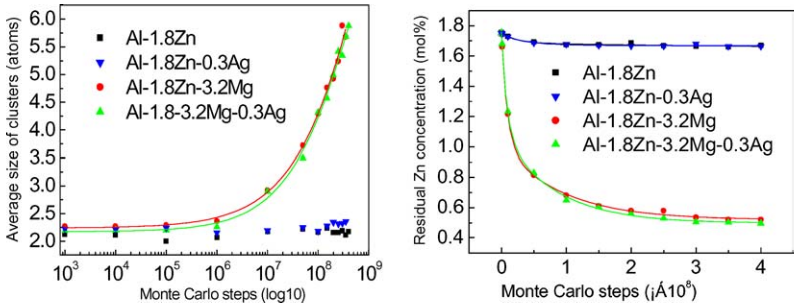
(d) blue, red, green and black circles represent Cu, Mg, Ag atoms and vacancies respectively

Figure 2 Typical atomic configurations on one atomic layer of (001) plane in (a) Al-Cu, (b) Al-Cu-Ag, (c) Al-Cu-Mg and (d) Al-Cu-Mg-Ag alloys simulated at 453 K for 4×10^8 MCs.



(a) (b)

Figure 3 Variations in vacancy-solute probability in Al-Cu (-Mg-Ag) alloys (a) and solute-solute probability in Al-Cu-Mg-Ag alloy (b) with MCs simulated at 453 K.



(a) (b)

Figure 4 Variations in average size of Zn clusters (a) and residual Zn concentrations in the matrix (b) with Monte Carlo steps for Al-Zn (-Mg-Ag) alloys simulated at 453 K.

micro-alloying elements in these alloys still remain unknown due to the difficulty of direct detection of atomic behavior. Here, we illustrate the role of Mg and Ag atoms in clusters formation in Al-Cu based alloys by atomic-scale simulations. Fig. 1 shows the variations of average size of Cu clusters and residual Cu concentrations in the matrix during dynamical evolution for Al-Cu (-Mg-Ag) alloys simulated at 453 K. The average size of Cu clusters in the Mg-added and Mg-Ag-co-added alloys tends to be significantly smaller than that in the Al-Cu and Ag-added alloys with increasing of Monte Carlo steps. The residual Cu concentration in the matrix displays a monotonous decrease at the same rate in both Ag-added alloy and Al-Cu alloy, whereas Cu atoms condensation is obviously retarded in the Mg-added and Mg-Ag-co-added alloys.

Fig. 2 shows typical atomic configurations on one atomic layer of (001) plane in Al-Cu (-Mg-Ag) alloys simulated at 453 K for 4×10^8 MCs. It could be clearly observed from Fig. 2c and d that the small amount of Mg significantly suppresses the clustering of Cu atoms, which is consistent with the results shown in Fig. 1. As illustrated in Fig. 3a, Mg atoms are frequently presented together with vacancies. The increased number of Mg-vacancy pairs in the Mg-added alloy is obviously responsible for the decrease of Cu diffusion, whereas Ag addition has almost no influence on the microstructural evolution of Al-Cu alloys as shown in Fig. 2b. These results could be verified by the experiments of electrical resistivity measurement and positron annihilation study [14–15]. A relative high number density of Mg-Cu-vacancy complexes are formed in both Al-Cu-Mg and Al-Cu-Mg-Ag alloys with the help of vacancies since Cu-Mg has a positive ordering parameter, and Ag atoms are preferentially bounded with Mg atoms in Mg-Ag-co-added alloy as shown in Figs 2d and 3b. These results indicate that the small amount of Ag may obviously affect the nucleation behavior of the Ω phase, in well agreement with the experimental conclusion that Ω phase was homogeneously distributed among the Al-Cu-Mg-Ag alloy, while only few Ω phases were detected in Al-Cu-Mg alloy [16–17].

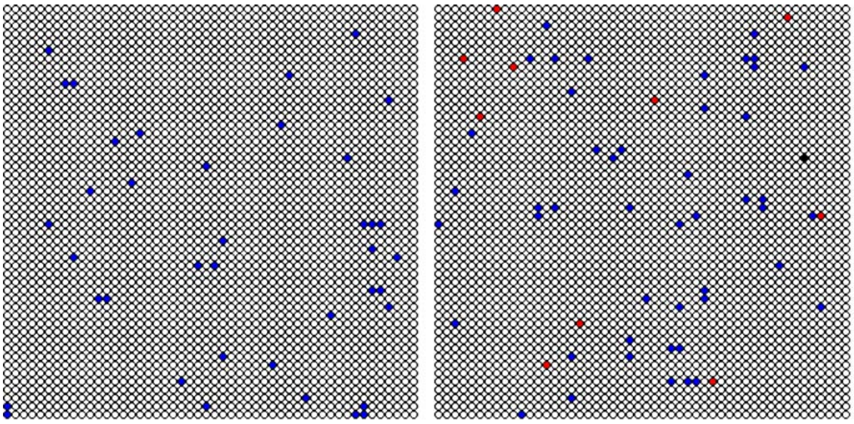
3.2. Al-Zn based alloys

Al-Zn based alloys with additions of Mg and Ag have been widely used as high strength structural materials. The present study is desired to examine the precise effects of Mg and Ag in these alloys by Monte Carlo simulations. Fig. 4 shows variations in average size of Zn clusters and residual Zn concentrations in the matrix during dynamical evolution for Al-Zn (-Mg-Ag) alloys simulated at 453 K. The average size of Zn clusters in the Mg-added and Mg-Ag-co-added alloys tends to be significantly larger than that in the Al-Zn and Ag-added alloys with increasing of Monte Carlo steps. The Mg-added and Mg-Ag-co-added alloys obvious favor the condensation of Zn atoms.

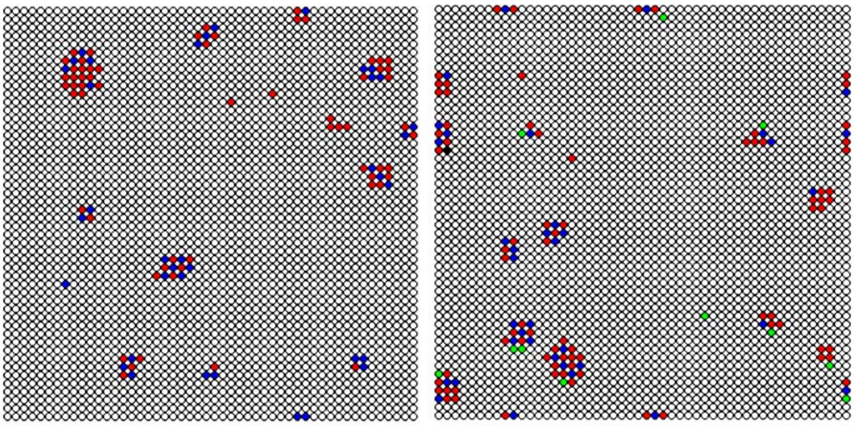
Fig. 5 shows typical atomic configurations on one atomic layer of (001) plane in Al-Zn (-Mg-Ag) alloys simulated at 453 K for 8×10^8 MCs. It is clearly

TABLE III Order parameters for different atomic pairs (KJ/mol)

	Cu-Mg	Cu-Ag	Mg-Ag	Zn-Mg	Zn-Ag
$\varepsilon_{\mathrm{dia}}$	0.45	2.40	−2.55	−12.45	1.5

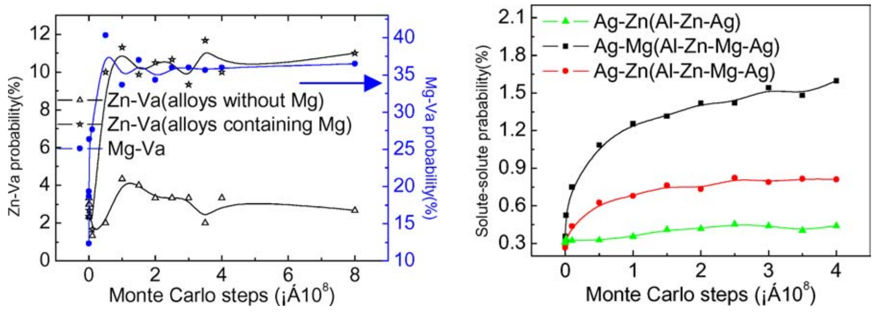


(a) Blue circle represents Zn atoms *(b) blue, red and black circles represent Zn, Ag atoms and vacancies respectively*



(c) Blue, red and black circles represent Zn, Mg atoms and vacancies respectively *(d) blue, red, green and black circles represent Zn, Mg, Ag atoms and vacancies respectively*

Figure 5 Typical atomic configurations on one atomic layer of (001) plane in (a) Al-Zn, (b) Al-Zn-Ag, (c) Al-Zn-Mg and (d) Al-Zn-Mg-Ag alloys simulated at 453 K for 8×10^8 MCs.



(a) (b)

Figure 6 Variations in vacancy-solute probability in Al-Zn (-Mg-Ag) alloys (a) and solute-solute probability in Al-Zn-Mg (-Ag) alloys (b) with MCs simulated at 453 K.

revealed from Fig. 5c and d that a small amount of Mg significantly promotes the clustering of Zn atoms by co-clustering of Mg-Zn-vacancy or Mg-Zn-Ag-vacancy. Combined with the results shown in Fig. 4, it can be concluded that the Mg-added alloys are favorable for Zn clustering due to the fast formation of Mg-Zn co-clusters. According to Table III, the order parameter of Zn-Mg atomic pair is much larger than those of others (in the case of $\varepsilon_{\text{dia}} < 0$, Zn atoms and Mg atoms are inclined to form intermetallic compounds). This result can also be deduced from Fig. 6a where vacancy-Zn probability in Mg-added alloys is much larger than that in other alloys without Mg. As for the effect of Ag, it can be found from Figs 6b and 5d that Ag atoms are participated to the Mg-Zn-vacancy complexes to form plenty of Mg-Zn-Ag co-clusters. These co-clusters are believed to act as favor nuclei from which the intermediate precipitate η' seems to have nucleated [6]. Moreover, unlike that in Al-Cu-Mg alloy, Ag atoms are found to interact with both Mg and Zn atoms in Al-Zn-Mg alloy by comparison between Figs 3b and 6b.

4. Conclusions

The role of micro-alloying elements Mg and Ag in Al-Cu and Al-Zn based alloys was investigated using Monte Carlo simulations. The microstructural evolution reproduced by the simulation model reveals not only the detailed formation mechanism of clusters, but also the atomistic behavior of the micro-alloying elements. The obtained conclusions are as follows:

(1) Small amount additions of Mg to the Al-Cu alloy markedly retard the formation of Cu clusters due to the preferential trapping of free-vacancies available for Cu diffusion.

(2) Additions of Mg to the Al-Zn alloy promote the formation of Zn clusters due to the preferential Mg-Zn interaction. Such situations can be frequently observed in atomic configurations during the simulation.

(3) In contrast, additions of Ag exert no marked influence on the formation kinetics of Cu clusters or Zn clusters in the Al-Cu alloy or Al-Zn alloy.

(4) In both Al-Cu-Mg and Al-Zn-Mg alloys, Ag atoms are preferentially bounded to Mg-Cu-vacancy and Mg-Zn-vacancy complexes respectively. However, in Al-Cu-Mg alloy Ag atoms interact with Mg, while in Al-Zn-Mg alloy with both Mg and Zn.

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